



# Analytical pyrolysis of biomass using gas chromatography coupled to mass spectrometry



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## ABSTRACT

Biofuels represent an important category of green and alternative energy, and they have high potential to meet the energy demands of society. They are obtained from various renewable sources, which include energy crops, wood and wood wastes, agricultural by-products, and algae. Pyrolysis is an advanced technology to produce biofuels from biomass. In this review, we focus on analytical pyrolysis of biomass, in which a sample is decomposed with the help of heat treatment in an inert atmosphere. In a Py-GC-MS system, the pyrolyzer unit is connected to a gas chromatograph with a mass detector. We provide insight into the analytical pyrolysis of various biomasses and biomass components, decomposition pathways, formation of possible decomposition products and the effects of catalysts in the degradation of biomasses. Also, we discuss sample preparation and instrumentation for analytical pyrolysis.

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## 1. Introduction

Biomass, an attractive natural material, is a green, alternative and renewable energy resource. Potential biomass resources are wood, energy crops, wood waste, agricultural byproducts, sewage sludge and algae. The effective use of biomass resources as an energy source has been the topic of many research projects throughout the past 20 years. The utilization of biomass for the production of second-generation biofuels and/or valuable chemicals is carried out using thermochemical conversion technologies, mainly pyrolysis and hydrothermal processes. The process in which organic matter is decomposed into simpler fragments with the assistance of heating in

the absence of oxygen is called pyrolysis. The process is irreversible and carried out at elevated temperatures (generally higher than 400°C).

There are two types of pyrolysis: analytical and applied. Applied pyrolysis is carried out for the purpose of producing pyrolysis compounds. After the process, each product (liquid, solid and gaseous) is analyzed using different methods [i.e., gas chromatography mass spectrometry (GC-MS), Fourier transform infrared (FTIR) spectrometry, nuclear magnetic resonance (NMR), elemental analysis, and gas chromatography with flame-ionization detection or thermal-conductivity detection (GC-FID or GC-TCD)]. Applied pyrolysis is not a rapid, time-saving technique. Analytical pyrolysis involves the characterization of the analyte by decomposition upon heat treatment in the absence of oxygen. Analytical pyrolysis has been used effectively for the decomposition of biomass and biomass components. This technique allows us to understand the decomposition

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pathway of biomasses. It also gives us important information about the role and the effects of catalysts during decomposition of biomass.

Direct analysis of biomasses, macromolecular and heterogeneous materials, is carried out using pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS). In this analytical technique, biomass is subjected to heat treatment and then volatiles and semi-volatiles are identified based on the mass spectra by means of GC-MS. Py-GC-MS is a very rapid, reliable technique to analyze pyrolysis products from the decomposition of biomasses.

In general, the main disadvantage of Py-GC-MS is that pyrolysis produces enormous amounts of components by cracking and by rearranging fragments. Biomass pyrolysis liquids (bio-oils) are complex mixtures containing a wide range of organic compounds. Although the composition of liquids may change, depending on the raw material and pyrolysis conditions (e.g., temperature, heating rate, and use of a catalyst), the liquids mainly comprise oxygenated hydrocarbons (i.e., phenols, aldehydes, ketones, acids, and esters). The heating values of liquids are lower than those obtained from fossil fuels due to the high oxygen content in biomass pyrolysis liquids. Py-GC-MS allows us to understand the formation of these compounds from the biomass. From this approach, there are many studies concerning the Py-GC-MS of biomasses and single biomass components (e.g., lignin and cellulose, protein and lipids) [1–4] and model compounds (e.g., sinapyl and coniferyl alcohol, glyceraldehyde, levoglucosan and chlorogenic acid) [5,6].

This review focuses on the Py-GC-MS of biomass and biomass components. We also discuss the use of various types of catalysts and their effects on biomass pyrolysis.

## 2. Instrumentation

### 2.1. Types of pyrolyzer

In a Py-GC-MS system, a pyrolyzer is connected directly to the injector port of a gas chromatograph (GC) with a mass detector (MS) (Fig. 1). The pyrolyzer unit facilitates the decomposition of organic materials into smaller fractions via chemical-bond cleavage in a macromolecular network with the assistance of heating. Smaller volatile fractions of organic materials are moved to the column with

the help of an inert gas (nitrogen or argon). The volatiles are separated in the column. Peak identifications are generally accomplished with the help of a mass spectral library.

Off-line pyrolysis in which the pyrolyzer is not connected to the GC instrument is also possible. In this type of pyrolysis, the analyte is first pyrolyzed and then analyzed by different analytical methods. These methods lead to the characterization of the analyte in detail and the attempt to provide more information about decomposition products. The process also allows us to prevent memory effects [7].

Although various types of pyrolyzer are applicable for use in a Py-GC-MS system, the micro-furnace, the Curie Point, and the resistively heated filament unit are among commonly used pyrolyzers [8].

In the micro-furnace system, the furnace is heated to the desired temperature and the analyte is injected into the pyrolysis zone using a syringe or a small cup [8]. Although the heating rate can be set in this pyrolyzer unit, it is difficult to maintain a fixed heating rate as the furnace generally heats slowly [8]. Two areas that need to be developed in this pyrolyzer unit are reproducibility and additional cooling of the system between runs.

In the Curie Point pyrolyzer unit, a ferromagnetic sample holder is used and the sample is then heated by a high-frequency induction coil [8]. The system has limited temperature-program capability as the heating of the system stops increasing when the Curie Point of the metal has been reached. The heating of the system is carried out in a few seconds.

Another type of pyrolyzer unit includes filaments in which both pyrolysis temperature and heating rate can be controlled with the assistance of a piece of resistive metal [8]. The heating is generated by an electric current which passes the metal through the resistive metal. The heating of the system continues until the desired temperature is reached and it is maintained by reducing the voltage [8].

### 3. Sample preparation

Less than 1 mg of the sample is required for Py-GC-MS analysis. One of the main drawbacks of the biomass-pyrolysis process is

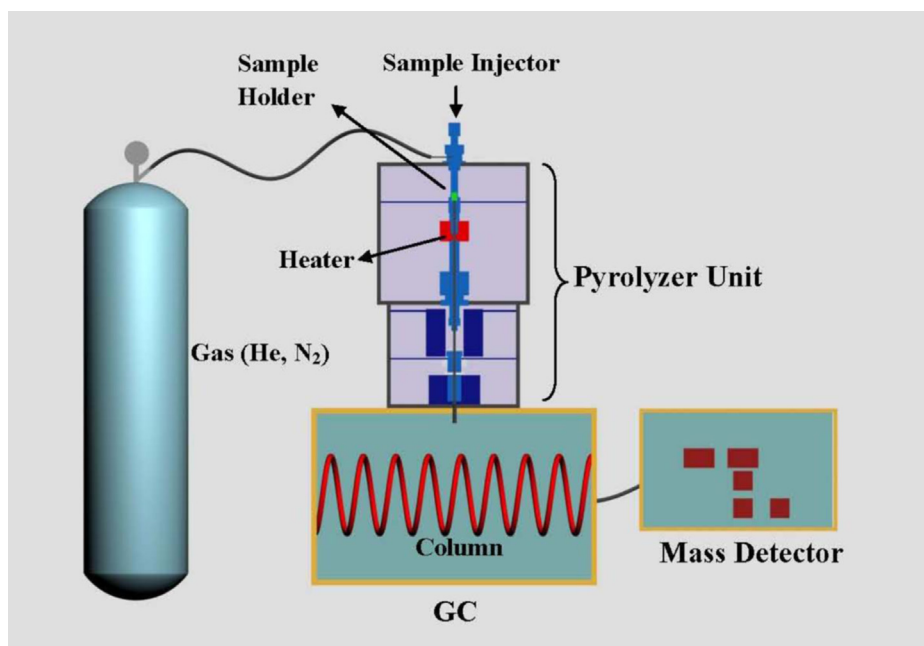


Fig. 1. A schematic diagram of Py-GC-MS instrument.

that the biomass feedstock should contain less than 10 wt% of moisture. In general, biomasses that have moisture higher than 10 wt% should be dried before Py-GC-MS is used. The drying process is an additional cost to take into account in industrial applications.

Some pretreatment of the analyte is necessary before Py-GC-MS. Extraction, which helps to remove extractives and inorganic species in biomass samples, is one of these pretreatment methods. Biomass samples were extracted in a Soxhlet apparatus using solvents having different polarities, such as dichloromethane, hexane, and ethanol.

Water extraction is also used in order to eliminate inorganic portions in the biomass [9]. Derivatization of analyte, also known as thermochemolysis, is a pretreatment method designed to avoid complications in analysis by producing a more volatile moiety. Different derivatization reagents are available, such as silylating, acylating, and alkylating reagents.

The most commonly used derivatization reagent for the analysis of biomass by Py-GC-MS is tetramethylammonium hydroxide (TMAH). The presence of phenyl-propanoid compounds causes complications for lignin analysis by Py-GC-MS [10], but use of TMAH solves this problem.

Rio et al. [11] investigated the analysis of different types of lignin and cinnamic acid by Py-GC-MS. They showed that the use of TMAH is an ideal method for the analysis of p-hydroxycinnamic acid, the amounts of which vary depending on the types of lignin analyzed.

Fabbri and colleagues [12] explored off-line pyrolysis/silylation coupled with GC-MS in order to determine anhydrosugars produced from cellulose and chitin in the form of trimethylsilyl (TMS) derivatives. The silylating reagents used in the study were hexamethyldisilazane (HMDS), trimethylsilyldiethylamine (TMSDEA), bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylsilylimidazole (TMSI). The primary product from the pyrolysis of cellulose was the derivative of levoglucosan (LG) corresponding to 2,3,4-tris-TMS ether for all tested silylating reagents. Off-line pyrolysis/silylation of chitin with HMDS produced 3,4-bis-TMS ether of 1,6-anhydro-2-acetamido-2-deoxyglucopyranose as a major product. As a result, we may conclude that derivatization is a useful, effective method to improve the detection of specific compounds from the analytical pyrolysis of biomass.

### 3.1. Py-GC-MS of carbohydrates

In this sub-section, we discuss studies concerning analytical pyrolysis of carbohydrates, such as cellulose, hemicellulose, chitin and glucose. As cellulose is the most abundant biopolymer on Earth [13], it has been widely investigated in analytical pyrolysis studies. Cellulose, a polysaccharide, is composed of glucose units connected to each other by the  $\beta$ -(1–4)-glycosidic bond. Pyrolysis of cellulose mainly yields pyrans, furans, and other small molecules, such as aldehydes and ketones. The composition and the quantities of cellulose pyrolysis products are affected by pyrolysis conditions (e.g., temperature, time, and catalyst). Pure cellulose, cellulose obtained from lignocellulosic biomass, and a model compound for cellulose (e.g., glyceraldehydes) have been used for analytical pyrolysis coupled with GC-MS [2,14,15].

Wang and co-workers [14] performed fast pyrolysis of cellulose, cellulose and glucose at 600°C for 10 s. Pyrolysis products from cellulose were similar to those of cellulose and glucose, and they yielded mainly pyrans, furans, acetic acid, aldehydes, ketones, and carbon dioxide. However, pyrolysis products of cellulose and glucose contained a higher amount of furan and a lower amount of pyran than those of cellulose. The primary pyrolysis product of all tested raw materials was furfural.

Lu et al. [2] carried out fast pyrolysis of cellulose at the temperatures of 300–700°C with residence times of 5 s, 10 s and 30 s. The compounds identified were anhydrosugars, furans, aldehydes

and ketones. The relative concentration of each product was strongly affected by both temperature and residence time. Two studies [2,14] reported that the set pyrolysis temperature was lower than the actual one (about 100°C) due to the poor thermal conductivity of cellulose.

Wei et al. [16] investigated analytical pyrolysis of cellulose using a Py-GC-MS and found a similar group of compounds (i.e., anhydrosugars, furans, aldehydes and ketones). Many reactions occurred during the pyrolysis of cellulose, such as dehydration, decarbonylation and decarboxylation. Anhydrosugars were observed as the first decomposition products of cellulose. They were also intermediates for other products, such as pyrans, furans, aldehydes, and ketones. It is also possible to get a target compound, such as hydroxylactone, levoglucosenone, and furfural at a high concentration from the pyrolysis of cellulose with the help of catalysts. Most efforts to produce special compounds at high concentrations have used pyrolysis of cellulose and different types of catalyst.

Fabbri and co-workers [13] used nanopowder metal oxides (titanium dioxide, aluminum oxide, and aluminum titanate) for the pyrolysis of cellulose at 350°C and 500°C for 60 s. It was shown that the yield of a chiral cyclic hydroxylactone (LAC) could be increased with nanopowder metal oxides at 350°C. The same group [17] also used various zeolites (H-Y, NH<sub>4</sub>-Y and NH<sub>4</sub>-ZSM-5 types) and nanopowder metal oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, TiSiO<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>TiO<sub>2</sub>) as catalysts for the pyrolysis of cellulose at 500°C for 60 s. All nanopowder metal oxides were found to increase the yields of anhydrosugars, whereas zeolites reduced the yields of anhydrosugars under identical conditions.

Lu and co-workers [18] investigated analytically pyrolysis of cellulose with sulfated metal oxides (SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>) at temperatures of 500°C, 600°C, 700°C and 800°C for 10 s. The products, such as levoglucosan (LGA) and hydroxyacetaldehyde (HAA), were significantly reduced or completely removed while the concentration of furans was significantly increased by the presence of catalysts. The tested catalysts showed different selectivities based on the target compounds. The same group [19] also investigated the effects of sulfated titania oxides on the pyrolysis of cellulose at different temperatures (300–500°C), residence times (5–20 s), cellulose/catalyst ratios (1–1/3), and TiO<sub>2</sub> crystal types (either anatase or rutile). The relative concentration of levoglucosenone (LGO) was the highest at the following conditions: pyrolysis temperature, 350°C; catalyst ratio, 1/3; and, using anatase TiO<sub>2</sub>. The residence time did not have a significant effect on the concentration of LGO.

Off-line pyrolysis of cellulose with and without montmorillonite K10 catalyst followed by GC-MS analysis was carried out at 350°C, 400°C, 450°C and 500°C at different cellulose/catalyst ratios (9, 3, and 1) and heating rates (10°C/min and 100°C/s) [20]. The use of this catalyst decreased the bio-oil yields; an increase in the amount of catalyst led to a decrease the bio-oil yields. The use of the catalyst promoted the formation of levoglucosenone (LGO), hydroxylactone (LAC) and 2-furfural (FF).

In another study, Rutkowski [21] investigated the catalytic effect of CuCl<sub>2</sub> and AlCl<sub>3</sub> (3–30 wt% of the raw material) at temperatures of 350–500°C with different heating rates (10 °C /min, and 100°C/s) on the pyrolysis of cellulose followed by GC-MS. The use of a catalyst (CuCl<sub>2</sub> or AlCl<sub>3</sub> at a concentration of 10 wt%) enhanced the gas products and decreased the bio-oil yields at 450°C. The yields of levoglucosenone, 1,4:3,6-dianhydro- $\alpha$ -d-glucopyranose, and unidentified anhydrosugars increased with catalysts at 450°C. To see the real cracking effect of a Lewis catalyst, such as AlCl<sub>3</sub>, low concentrations (0.1–1.0 wt% of the raw material) and the lowest temperatures (e.g., 300°C) are necessary for any type of biomass [22]. The cracking ability and changes in bio-oil composition can be seen at the lowest temperature (300°C) and concentration of the catalyst (0.1–1.0 wt% of the raw material) when compared with the

**Table 1**

Key compounds from the pyrolysis of cellulose followed by GC-MS. {Adapted from [23]}

Compounds
Acetone
Hydroxyacetone
Hydroxyacetaldehyde
Furfural
Anhydro-d-mannose
5-(Hydroxymethyl)furfural (HMF)
Levogluconan

non-catalytic run (at 500°C). The products likely to occur from the non-catalytic pyrolysis of cellulose are tabulated in Table 1 [23]. The bio-oil compositions alter, depending on both the types and the amounts of catalysts used in Py-GC-MS.

### 3.2. Py-GC-MS of lignin

Lignin, a second major component of lignocellulosic biomass, consists of phenyl propane units bonded to each other via  $\alpha$ - and  $\beta$ -alkyl aryl ether bonds. Considerable effort on the analytical pyrolysis of lignin with and without catalysts has been made to understand decomposition pathways and formation of products. Analytical pyrolysis of lignin gives mainly phenolic compounds [24]. Identified compounds from the pyrolysis of lignin followed by GC-MS are shown in Table 2.

The concentration of pyrolysis products alters, depending on the type of lignin. A wheat-straw lignin was subjected to Py-GC-MS at 500°C for a residence time of 1 min [25]. The identified key compounds were found to be derivatives of basic lignin units (guaiacyl, syringyl, and hydroxyphenyl). Guaiacyl units were the dominant pyrolysis products. The fast pyrolysis of three different types of lignin (Aspen, Kraft and Prairie cordgrass) was carried out at 600°C with a heating rate of 1000°C/s and held for 1 min [26]. According to normalized absolute areas, the major products were syringol,

4-vinyl guaiacol, guaiacol for Aspen lignin, lignin derived from Prairie cordgrass, and Kraft lignin, respectively.

The determination of the ratio of syringyl and guaiacyl units (S/G ratio) in lignin from different parts of *Eucalyptus camaldulensis* was carried out at 450°C by Py-GC [24]. The key peaks derived from the syringyl and guaiacyl units could be determined by Py-GC with high reproducibility and a relative standard deviation less than 2%. The S/G ratio was found to be high at the pith side and it showed a gradual decrease towards the bark in the radial direction.

Rahmi et al. [1] determined the Klason lignin content and lignin-degradation products by Py-GC-MS. The characteristic peaks from the three major lignin subunits (G: guaiacyl lignin; S: syringyl lignin; H: hydroxyphenyl lignin) were identified and statistically correlated to predict the Klason lignin content of a collection of *Lolium* and *Festuca* grasses. The Klason lignin content was in the range 2.1–3.7% with a high correlation coefficient ( $R^2 = 0.88$ ).

The S/G ratio in the lignin content of different non-woody plants (hemp, flax, jute, sisal and abaca) was determined by Py-GC-MS with and without the use of TMAH and by FTIR after alkaline isolation [11]. The S/G ratio was in the range 0.4–3.4, depending on the type of biomass. Lignin from hemp and flax had low S/G ratios, while jute, sisal and abaca had high S/G ratios.

The acid-precipitable polymeric lignin obtained from wheat straw transformed by selected *Streptomyces* strains was analyzed Py-GC-MS [27]. The S/G ratio was found to be 0.60–0.90 in samples harvested with NaOH and in the range 0.53–1.47 in samples harvested with water.

Py-GC-MS conditions (i.e., pyrolysis temperature, heating rate, and the use of catalysts) had important effects on the distribution and concentration of each product in the pyrolytic liquids. The effects of Py-GC-MS conditions (i.e., heating rates, 2.6–120°C/s; pyrolysis temperatures, 500°C and 800°C; and, different atmospheres: N<sub>2</sub>, H<sub>2</sub>, and mixtures of N<sub>2</sub> and acetylene) on product yields for different lignin samples were investigated [28]. Lower liquid and gaseous yields and higher amounts of cokes were obtained at 500°C. The effects of hydrogen and acetylene were also significant.

The effects of NaCl and zeolite on the Py-GC-MS of lignin from the isolated enzymatic/mild acidolysis of bamboo at different temperatures (320–800°C) were investigated [29]. The use of NaCl produced a high amount of bio-oil and bio-gas and a low yield of coke while zeolite-promoted coke formation. The relative concentration of each compound underwent changes contingent upon the type of catalyst.

Lignin obtained from four different sources was subject to the Py-GC-MS with and without catalysts (HZSM-5 or CoO/MoO<sub>3</sub>) [30]. The use of a catalyst (HZSM-5 or CoO/MoO<sub>3</sub>) increased the aromatic content. However, the increase in aromatic content that was greater in the case of HZSM-5 can be explained by the different degradation pathways.

### 3.3. Py-GC-MS of lignocellulosic biomass

Py-GC-MS of lignocellulosic biomass allows us to observe degradation pathways and the origins of products. Gao et al. [31] reported on the pyrolysis of pine sawdust at 700°C using Py-GC-MS. The pyrolysis products mainly comprised gaseous (i.e., CH<sub>4</sub>, CO, and CO<sub>2</sub>) and other compounds (i.e., acetaldehyde, acetic acid, and acetic formic anhydride).

Py-GC-MS of lignocellulosic biomass was carried out at 350°C under oxidizing conditions for 30 s, 45 s, 60 s, 75 s and 90 s, in order to observe the stages of formation and degradation of charred residues [32]. The results demonstrated that the aromaticity of charred products increased in the early heating stages. However, it showed a decrease in the advanced heating stages. Charred residues after

**Table 2**

Key compounds from the pyrolysis of lignin followed by GC-MS. {Adapted from [24]}

Compounds	Origin
Guaiacol	G
4-Methylguaiacol	G
Vinylguaiacol	G
Syringol	S
Eugenol	G
Vanillin	G
cis-Isoeugenol	G
Methylsyringol	S
Homovanillin	G
trans-Isoeugenol	G
Acetoguaiacone	G
Guaiacylacetone	G
Vinylsyringol	S
Allylsyringol	S
Syringaldehyde	S
cis-Propenylsyringol	S
cis-Coniferyl alcohol	G
Homosyringaldehyde	S
trans-Propenylsyringol	S
trans-Coniferylaldehyde	G
Acetosyringone	S
trans-Coniferyl alcohol	G
Syringylacetone	S
cis-Sinapyl alcohol	S
trans-Sinapaldehyde	S
trans-Sinapyl alcohol	S

S = Syringyl unit, and G = Guaiacyl unit.



severe heating (carbon loss ~50%) contained substantial concentrations of structural components of plants.

Py-GC-MS of *Miscanthus x giganteus* was carried out at 520°C with a heating rate of 20°C/ms [33]. The product yields of pyrolysis altered, depending on the time of harvest and the duration of the storage of *Miscanthus x giganteus*. The compounds were identified as acids, alcohols, ketones, and furans.

The studies concerning Py-GC-MS of lignocellulosic biomass mainly focused on the use of various catalysts in order to observe the effects on the bio-oil yields or specific groups, such as phenols, aromatics, and acids.

Py-GC-MS of cell-wall components [e.g., cellulose, hemicellulose (oat spelt xylan), lignin (Organosolv), and model compounds (e.g., levoglucosan and chlorogenic acid)] was carried out at 500°C in the absence and the presence of potassium [6]. Although the effects of potassium on the pyrolysis products were altered, depending on the type of raw material used, the char yield increased for all tested raw materials.

Fast pyrolysis of cassava rhizome in the presence of a zeolite catalyst (ZSM-5), two aluminosilicate mesoporous materials (Al-MCM-41 and Al-MSU-F), and a commercial alumina-stabilized ceria catalyst (MI-575) was carried out by Py-GC-MS [34]. The effects of catalysts on the relative concentration of aromatic hydrocarbons, phenols, lignin-derived compounds, carbonyls, methanol and acetic acid were investigated. All catalysts produced aromatic hydrocarbons. They also produced a decrease in oxygenated lignin compounds, which was an indication of improving bio-oil quality.

In the study by Mochizuki et al. [35], the effect of SiO<sub>2</sub> pore size on pyrolysis residues of *Jatropha* was investigated using Py-GC-MS. The pyrolysis experiments were completed at 500°C and the tested catalysts had different pore sizes: SiO<sub>2</sub>-Q3, -Q10, -Q30 and -Q50 with pore diameters of 3 nm, 16 nm, 45 nm and 68 nm, respectively. The SiO<sub>2</sub>-Q10 catalyst showed the highest activity in terms of decreasing solid-residue yields and removing oxygenated hydrocarbons (such as, acids, ketones, and aldehydes).

The same group [36] reported the effects of zeolites H-USY, H-Mordenite, H-Beta, and H-ZSM-5 on pyrolysis products from *Jatropha* husk and cedar wood using Py-GC-MS. The pyrolysis experiments were carried out at 500°C. The aromatic content of pyrolytic liquids from *Jatropha* husk was higher than those obtained from cedar wood in the catalytic runs. H-USY catalyst showed the highest selectivity on monocyclic aromatic hydrocarbons.

Py-GC-MS of sawdust in the presence of SBA-15 catalyst and four Al/SBA-15 catalysts with different Si/Al ratios was carried out at 600°C [37]. The yields of pyrolytic liquids decreased with the use of all tested catalysts. The cracking ability of Al/SBA-15 catalysts increased when the Si/Al ratios decreased. All of the catalysts tested led to a significant diminution in the levoglucosan yield.

### 3.4. Py-GC-MS of algal biomass

Algal biomasses, mainly composed of lipids, carbohydrates and proteins, have high potential to meet energy demands. The amount of each component varies depending upon the type of algae, including microalgae, cyanobacteria and macroalgae. As algal biomass has high water content, the studies concerning algal biomass generally focus on the hydrothermal processes. However, there are also a few studies that deal with Py-GC-MS of algal biomass, and are useful to understand decomposition pathways and formation of key compounds.

The four main carbohydrates (alginic acid, mannitol, laminarin and fucoidan) of brown macro-algae were studied at the temperature range 200–800°C by Py-GC-MS [38]. The main volatiles were furfural for alginic acid, 1-(2-furanyl) ethanone and dianhydromannitol for mannitol, 1,2-cyclopentanedione, 2-hydroxy-3-methyl 2-cyclopenten-1-one, and acetic acid for laminarin. The

**Table 3**

Identified compounds from brown algae using Py-GC-MS [39]

Compounds
2,3-butanedione
2,5-dimethylfuran
Acetic acid
N-nitrosodimethylamine
1-hydroxy-2-propanone
Toluene
3-hydroxybutanone
Propanoic acid
Pyrrole
Styrene
Furfural
2-propylfuran
2-methyl-1H-pyrrole
1-(2-furanyl)ethanone
1,2-cyclopentanedione
5-methyl-2-furancarboxaldehyde
3-acetyldihydro-2(3H)-furanone
2-hydroxy-3-methyl-2-cyclopenten-1-one
2-methoxy-5-methylthiophene
Phenol
4-methylphenol
2,5-dimethylphenol
3-ethylphenol
Isomannide
Pyridinol
2-methyl-2-propenoic acid ethyl ester
Indole
Isosorbide
Nitrogen-containing compounds

identified compounds from brown algae using Py-GC-MS are shown in Table 3 [39].

Py-GC-MS of microalgae obtained at different culture conditions was investigated by Valdes et al. [40]. Semi-quantitative determination of each component of the microalgae was estimated using Py-GC-MS and the linear regression was found to be  $R^2 = 0.75$  for proteins,  $R^2 = 0.85$  for lipids and  $R^2 = 0.95$  for carbohydrates.

Previous studies on the use of catalysts for Py-GC-MS of algal biomass were mainly concerned with the use of HZSM-5. The use of HZSM-5 catalyst in the conversion of any type of biomass significantly improves the aromatic content of pyrolysis vapors. Research on the conversion of microalgae into aromatic hydrocarbons and ammonia was carried out at 400–800°C in the presence of HZSM-5 using a micro-furnace pyrolyzer coupled with GC-MS [41]. Aromatic hydrocarbons were mostly benzene, toluene and xylene, and were obtained with a maximum carbon yield of 24 wt% and total aromatic selectivity of 75%.

The Py-GC-MS of microalgae with and without HZSM-5 catalyst was carried out at the temperature of 550°C [42]. The results showed that the carbon yield of aromatic hydrocarbons increased in the range 0.9–25.8 wt.% when the catalyst /biomass ratio was changed in the range 1:0–1:9.

The pyrolysis of microalgae and their main components (carbohydrates, proteins, and lipids) was carried out at 450–600°C using HZSM-5 [3]. Cellulose, egg whites, and canola oil were chosen as model compounds for carbohydrates, proteins, and lipids, respectively. The use of HZSM-5 catalyst improved the aromatic content of the pyrolysis oils for all feedstock, maximized at a catalyst to biomass ratio of 5:1. The aromatic content for model compounds at all tested conditions were in the following order: lipids > carbohydrates > proteins.

Torri et al. [43] upgraded bio-oils obtained from the hydrothermal treatment of microalgae in the presence of HZSM-5 using Py-GC-MS at 600°C. HZSM-5 catalyst showed not only deoxygenating activity but also denitrogenation activity. The Py-GC-MS of

microalgae produced a mixture of aromatic and aliphatic hydrocarbons with a maximum yield of ~50%.

#### 4. Conclusion

This review discussed Py-GC-MS of biomass to obtain biofuels. The complex nature of various types of biomasses can be analyzed using Py-GC-MS. The effect of catalysts on the degradation products from biomass can be investigated by means of Py-GC-MS. This technique is a useful tool to obtain fundamental knowledge regarding the influence of pyrolysis conditions on pyrolysis products (especially biofuels). It is also useful for obtaining information about the effects of catalysts on yields of pyrolysis products and identification of compounds. Also, we can infer the degradation pathways of various types of biomasses and determine optimal conditions for the high biofuel yields and/or high selectivity on the target compounds. These processes will help us determine the most effective industrial applications of biomass pyrolysis.

#### References

- [1] R. Fahmi, A.V. Bridgwater, S.C. Thain, I.S. Donnison, P.M. Morris, N. Yates, Prediction of Klason lignin and lignin thermal degradation of Lolium and Festuca grasses, *J. Anal. Appl. Pyrolysis* 80 (2007) 16–23.
- [2] Q. Lu, X. Yang, C. Dong, Z. Zhang, X. Zhang, X. Zhu, Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: analytical Py-GC-MS study, *J. Anal. Appl. Pyrolysis* 92 (2011) 430–438.
- [3] Z. Du, B. Hu, X. Ma, Y. Cheng, Y. Liu, X. Lin, et al., Catalytic pyrolysis of microalgae and their three major components: carbohydrates, proteins, and lipids, *Bioresour. Technol.* 130 (2013) 777–782.
- [4] Y. Wu, Z. Zhao, H. Li, F. He, Low temperature pyrolysis characteristics of major components of biomass, *J. Fuel Chem. Tech.* 37 (2009) 427–432.
- [5] A.E. Harman-Ware, M. Crocker, A.P. Kaur, M.S. Meier, D. Kato, B. Lynn, Pyrolysis-GC-MS of sinapyl and coniferyl alcohol, *J. Anal. Appl. Pyrolysis* 99 (2013) 161–169.
- [6] D.J. Nowakowski, J.M. Jones, Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds, *J. Anal. Appl. Pyrolysis* 83 (2008) 12–25.
- [7] C. Torri, D. Fabbri, Application of off-line pyrolysis with dynamic solid-phase microextraction to the GC-MS analysis of biomass pyrolysis products, *Microchem. J.* 93 (2009) 133–139 and references therein.
- [8] K.L. Sobiech, M. Baron, J. Gonzalez-Rodriguez, Recent trends and developments in pyrolysis-gas chromatography, *J. Chromatogr. A* 1186 (2008) 51–66.
- [9] E. Mészáros, E. Jakab, G. Várhegyi, TG/MS, Py-GC-MS and THM-GC-MS study of the composition and thermal behavior of extractive components of Robinia pseudoacacia, *J. Anal. Appl. Pyrolysis* 79 (2007) 61–70 and references therein.
- [10] J.C. del Rio, F. Martin, F.J. Gonzalez-Vila, Thermally assisted hydrolysis and alkylation as a novel pyrolytic approach for the structural characterization of natural biopolymers and geomacromolecules, *Trends Anal. Chem.* 15 (1996) 70–79.
- [11] J.C. del Rio, A. Guriérrez, I.M. Rodríguez, D. Ibarra, Á.T. Martínez, Composition of non-woody plant lignins and cinnamic acids by Py-GC-MS, Py/TMAH and FT-IR, *J. Anal. Appl. Pyrolysis* 79 (2007) 39–46.
- [12] D. Fabbri, S. Prati, I. Vassura, G. Chiavari, Off-line pyrolysis/silylation of cellulose and chitin, *J. Anal. Appl. Pyrolysis* 68–69 (2003) 163–171.
- [13] D. Fabbri, C. Torri, I. Mancini, Pyrolysis of cellulose catalysed by nanopowder metal oxides: production and characterisation of chiral hydroxylactone and its role as building block, *Green Chem.* 9 (2007) 1374–1379.
- [14] S. Wang, X. Guo, T. Liang, Y. Zhou, Z. Luo, Mechanism research on cellulose pyrolysis by Py-GC-MS and subsequent density functional theory studies, *Bioresour. Technol.* 104 (2012) 722–728.
- [15] G. Lv, S. Wu, Analytical pyrolysis studies of corn stalk and its three main components by TG-MS and Py-GC-MS, *J. Anal. Appl. Pyrolysis* 97 (2012) 11–18.
- [16] X. Wei, Q. Lu, X. Sui, Z. Wang, Y. Zhang, Characterization of the water-insoluble pyrolytic cellulose from cellulose pyrolysis oil, *J. Anal. Appl. Pyrolysis* 97 (2012) 49–54.
- [17] D. Fabbri, C. Torri, V. Baravelli, Effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose: an analytical study, *J. Anal. Appl. Pyrolysis* 80 (2007) 24–29.
- [18] Q. Lu, W.M. Xiong, W.Z. Li, Q.X. Guo, X.F. Zhu, Catalytic pyrolysis of cellulose with sulphated metal oxides: a promising method for obtaining high yield of light furan compounds, *Bioresour. Technol.* 100 (2009) 4871–4876.
- [19] Q. Lu, X.-M. Zhang, Z.-B. Zhang, Y. Zhang, Z.-F. Zhu, C.-Q. Dong, Catalytic fast pyrolysis of cellulose mixed with sulfated titania to produce levoglucosenone: analytical Py-GC-MS study, *Bioresour. Technol.* 122 (2012) 2820–2834.
- [20] P. Rutkowski, Pyrolytic behavior of cellulose in presence of montmorillonite K10 as catalyst, *J. Anal. Appl. Pyrolysis* 98 (2012) 115–122.
- [21] P. Rutkowski, Catalytic effects of copper(II) chloride and aluminum chloride on the pyrolytic behavior of cellulose, *J. Anal. Appl. Pyrolysis* 98 (2012) 86–97.
- [22] M.K. Akalın, S. Karagöz, Pyrolysis of tobacco residue part 2: catalytic, *Bioresour. Technol.* 111 (2011) 1773–1805.
- [23] D.K. Shen, S. Gu, A.V. Bridgwater, The thermal performance of the polysaccharides extracted from hardwood: cellulose and hemicellulose, *Carbohydr. Polym.* 82 (2010) 39–45.
- [24] H. Yokoi, Y. Ishida, H. Ohtani, S. Tsuge, T. Sonoda, T. Ona, Characterization of within-tree variation of lignin components in Eucalyptus camaldulensis by pyrolysis-gas chromatography, *Analyst* 124 (1999) 669–674.
- [25] Q. Yang, S. Wu, R. Lou, G. Lv, Analysis of wheat straw lignin by thermogravimetry and pyrolysis-gas chromatography/mass spectrometry, *J. Anal. Appl. Pyrolysis* 87 (2010) 65–69.
- [26] M. Zhang, F.L.P. Resende, A. Moutsoglou, D.E. Rayne, Pyrolysis of lignin extracted from prairie cordgrass, aspen, and Kraft lignin by Py-GC-MS and TGA/FTIR, *J. Anal. Appl. Pyrolysis* 98 (2012) 65–71.
- [27] J. Rodríguez, M.J. Hernández-Coronado, M. Hernández, P. Bocchini, G.C. Galletti, M.E. Arias, Chemical characterization by pyrolysis/gas chromatography/mass spectrometry of acid-precipitable polymeric lignin (APPL) from wheat straw transformed by selected streptomyces strains, *Anal. Chim. Acta* 345 (1997) 121–129.
- [28] M. Windt, D. Meier, J.H. Marsman, H.J. Heeres, S. de Koning, Micro-pyrolysis of technical lignins in a new modular rig and product analysis by GC-MS/FID and GCxGC-TOFMS/FID, *J. Anal. Appl. Pyrolysis* 85 (2009) 38–46.
- [29] R. Lou, S. Wu, G. Lv, Effect of conditions on fast pyrolysis of bamboo lignin, *J. Anal. Appl. Pyrolysis* 89 (2010) 191–196.
- [30] C.A. Mullen, A.A. Boateng, Catalytic pyrolysis-GC-MS of lignin from several sources, *Fuel Process. Technol.* 91 (2010) 1446–1458.
- [31] N. Gao, A. Li, C. Quan, L. Du, Y. Duan, TG-FTIR and Py-GC-MS analysis on pyrolysis and combustion of pine sawdust, *J. Anal. Appl. Pyrolysis* 100 (2013) 26–32.
- [32] F.J. González-Vila, P. Tinoco, G. Almendros, F. Martin, Pyrolysis-GC-MS analysis of the formation and degradation stages of charred residues from lignocellulosic biomass, *J. Agric. Food Chem.* 49 (2001) 1128–1131.
- [33] C.E. Greenhalf, D.J. Nowakowski, N. Yates, I. Shield, A.V. Bridgwater, The influence of harvest and storage on the properties of and fast pyrolysis products from *Miscanthus x giganteus*, *Biomass Bioenerg.* 56 (2013) 247–259.
- [34] A. Pattiya, J.O. Titiloye, A.V. Bridgwater, Fast pyrolysis of cassava rhizome in the presence of catalysts, *J. Anal. Appl. Pyrolysis* 81 (2008) 72–79.
- [35] T. Mochizuki, D. Atong, S.Y. Chen, M. Toba, Y. Yoshimura, Effect of SiO<sub>2</sub> pore size on catalytic fast pyrolysis of Jatropha residues by using pyrolyzer-GC-MS, *Catal. Commun.* 36 (2013) 1–4.
- [36] T. Mochizuki, D. Atong, S.Y. Chen, M. Toba, Y. Yoshimura, Pyrolyzer-GC-MS system-based analysis of the effects of zeolite catalysts on the fast pyrolysis of Jatropha husk, *App. Catal. A-Gen.* 456 (2013) 174–181.
- [37] L. Qiang, L. Wen-zhi, Z. Dong, Z. Xi-feng, Analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS) of sawdust with Al/SBA-15 catalysts, *J. Anal. Appl. Pyrolysis* 84 (2009) 131–138.
- [38] K. Anastasakis, A.B. Ross, J.M. Jones, Pyrolysis behavior of the main carbohydrates of brown macro-algae, *Fuel* 90 (2011) 598–607.
- [39] A.B. Ross, K. Anastasakis, M. Kubacki, J.M. Jones, Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC-MS and TGA, *J. Anal. Appl. Pyrolysis* 85 (2009) 3–10.
- [40] F. Valdés, L. Catalá, M.R. Hernández, J.C. García-Quesada, A. Marcilla, Thermogravimetry and Py-GC-MS techniques as fast qualitative methods for comparing the biochemical composition of *Nannochloropsis oculata* samples obtained under different culture conditions, *Bioresour. Technol.* 131 (2013) 86–93.
- [41] K. Wang, R.C. Brown, Catalytic pyrolysis of microalgae for production of aromatics and ammonia, *Green Chem.* 15 (2013) 675–681.
- [42] S. Thangalazhy-Gopakuman, S. Adhikari, S.A. Chattanathan, R.B. Gupta, Catalytic pyrolysis of green algae for hydrocarbon production using H<sup>+</sup>ZSM-5 catalyst, *Bioresour. Technol.* 118 (2012) 150–157.
- [43] C. Torri, D. Fabbri, L. Garcia-Alba, D.W.F. Brilman, Upgrading of oils derived from hydrothermal treatment of microalgae by catalytic cracking over H<sup>+</sup>ZSM-5: a comparative Py-GC-MS study, *J. Anal. Appl. Pyrolysis* 101 (2013) 28–34.